

Conditions for Obtaining Ultrafiltration Membranes from a Solution of Polyacrylonitrile in Dimethylformamide in the Presence of Formamide

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SYNOPSIS

The possibility to obtain ultrafiltration polyacrylonitrile terpolymer membranes in the presence of formamide in dimethylformamide polymer solution was studied. Correlation between the changes in viscosity and rheological characteristics of the polymer solutions, on the one hand, and the equivalent pore radii, efficiency, and selectivity of membranes, on the other hand, were found. The concentration of formamide was varied from 0 to 4 mass %. The dynamic characteristics of the membranes were determined with regard to calibrators having different molecular weight. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The preparation of ultrafiltration (UF) membranes by dry-wet casting depends not only on the polymer characteristics and the casting conditions but also on the structure, composition, and phase state of the polymer solutions as well. Bodzecz et al.¹ studied the phase diagram of the system polyacrylonitrile (PAN)-dimethylformamide (DMF)-coagulant and described membrane preparation from solutions containing 15–20 mass % polymer. Although there are differences in the composition of PAN-copolymer systems, this phase diagram can be applied to most of them. The phase state of a polymer solution is an important structure-determining factor. Different phase states lead to different membrane formation rates at a constant composition of the coagulation bath. The farther from the phase-transition boundary the composition of a polymer solution is, the greater the speed is and vice versa.

Our former studies² showed that the term "phase interval" could be used instead of "phase boundary." A section of the phase-state diagram indicates high stability of the solutions and a very slow transition toward pore formation. This state can be achieved by means of structure-forming substances possessing different coagulation ability.

At the same time, the smallest particles in the highly concentrated polymer solution may prove to be macromolecular aggregates and not macromolecules.^{3,4} Their arrangement and stability substantially affect membrane characteristics.⁵

The aim of the present research was to study the characteristics of solutions of PAN in DMF and the properties of the resulting semipermeable membranes. Different coagulants were used to change the phase state of the solutions slowly.

EXPERIMENTAL

Experiments were carried out with a PAN copolymer containing 92% acrylonitrile, 7% methyl methacrylate, and 1% vinylsulfonate. Its average molecular weight was $M_w = 63,000$. The solvent was DMF. Lithium nitrate, water, and formamide were used as structure-forming substances.

The rheological characteristics of the casting solutions were tested by a REOTEST II rotation viscometer (Germany) within 5 h after preparation. All UF membranes were cast within 10 h after the solutions were prepared. The membranes were cast onto an FO 2403 polyester nonwoven support (Viledon Filter, Germany). The membrane thickness was 0.3 mm. Their porosity was measured by a Carlo Erba 100 Hg porosimeter (Italy). Electron micro-

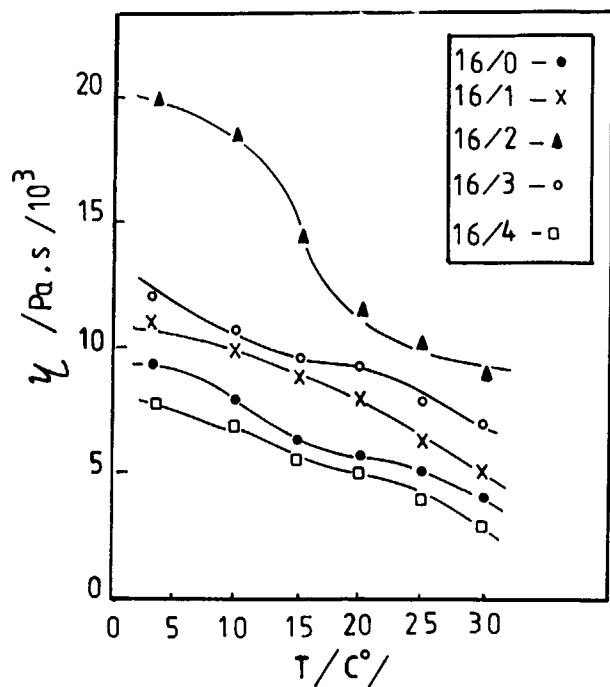


Figure 1 Effect of temperature on viscosity for 16 mass % polymer solutions of different formamide concentrations.

graphs were obtained by a Tesla-BS 340 electron microscope (Czech Republic).

Membrane efficiency and performance characteristics were determined by a SARTORIUS-SM 16526 laboratory cell (England). Human serum "albumin" ($M_w = 67,000$) and polyhydrates "Dextran" ($M_w = 10,000, 40,000, 70,000$) produced by "Fluka" were used as calibrators. The concentrations of albumin and polycarbohydrate were determined spectrophotometrically at wave lengths $\lambda = 280$ and 490 nm, respectively.

To characterize the composition of the casting solutions and the membranes formed, the ratio $A : B$ was used in the discussion, where A and B are the PAN copolymer and formamide concentrations in the solution, respectively. The concentrations of other structure-forming substances, LiNO_3 (2%) and water (1%), were kept constant for all systems used.

RESULTS AND DISCUSSION

Water and formamide are known to be coagulants for the system PAN-DMF. It is also known that water has better coagulation ability than that of formamide. Therefore, at a constant concentration of water in the polymer solution, the phase state of

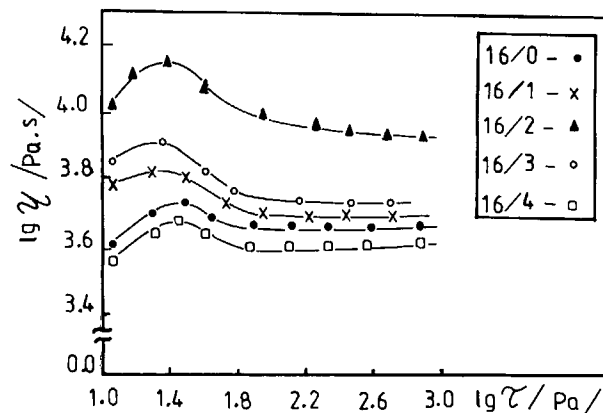


Figure 2 Effect of shear stress on viscosity for 16 mass % polymer solutions of different formamide concentrations.

the solutions can be changed more slowly by increasing the amount of formamide.

Formamide is often used to form microfiltration membranes from polymer solutions^{6,7} because it changes the solution viscosity to obtain a more symmetrical membrane structure. It should be expected that an increase of the formamide concentration will result in an increase of the polymer solution viscosity. In our case, however, this is true only for solutions containing no more than 2 mass % formamide (Fig. 1). At higher concentrations of formamide, viscosity decreases. The rheological curves, which have an exponential nature, show this maximum clearly. A tendency of congruity of viscosity rates of different solutions was not established at increasing temperatures. This dependence of the maxima on viscosity and temperature was also observed for so-

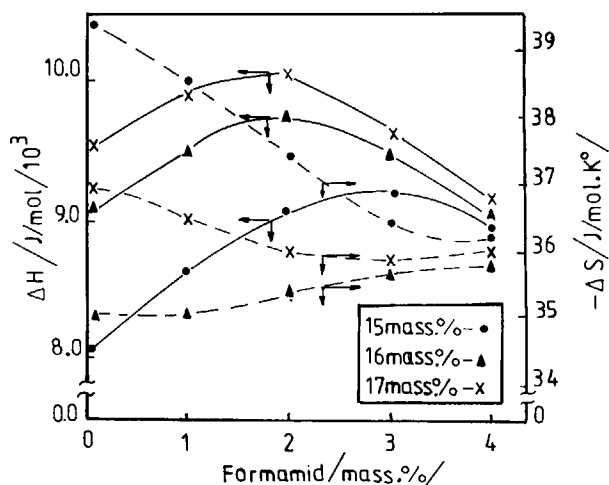


Figure 3 Dependencies in enthalpy and entropy of solutions of different PAN and formamide concentrations.

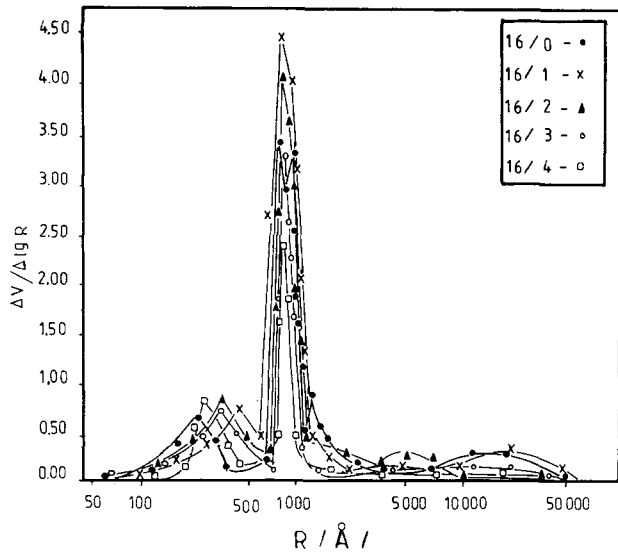


Figure 4 Differential curves of pore-size distribution in membranes obtained from 16 mass % PAN solutions different formamide concentrations.

lutions containing 15 and 17 mass % PAN. The maxima are at 3 and 1 mass % formamide, respectively. Obviously, the polymer concentration is another important factor in the membrane-formation process.

In 24 h, the solutions of lower viscosity, due to the presence of formamide, turn into a nonhomogeneous gel system which is not a solid phase.

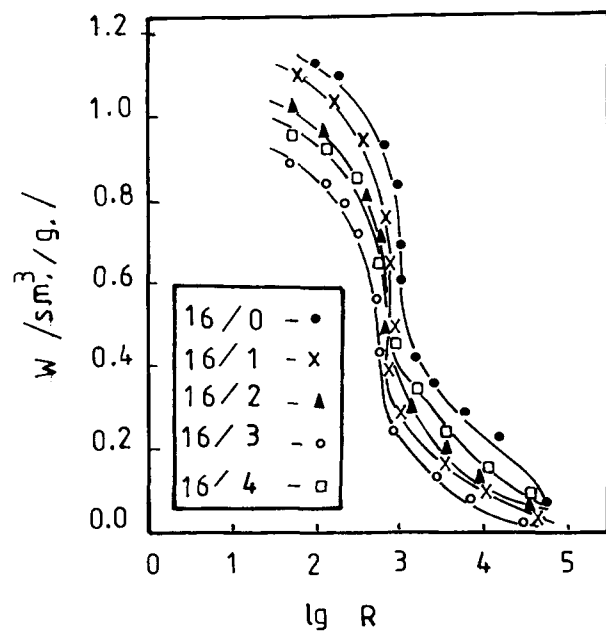
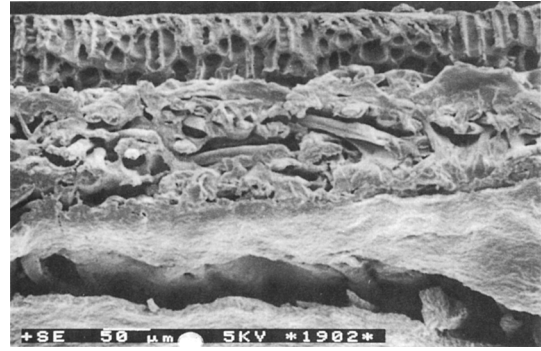
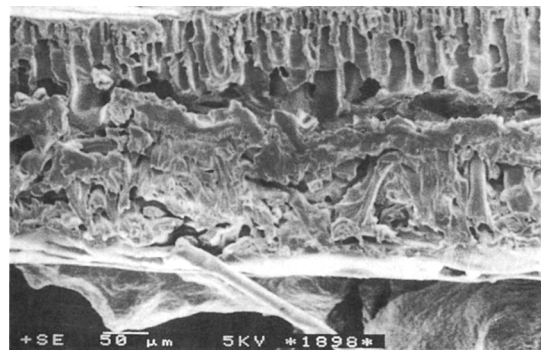


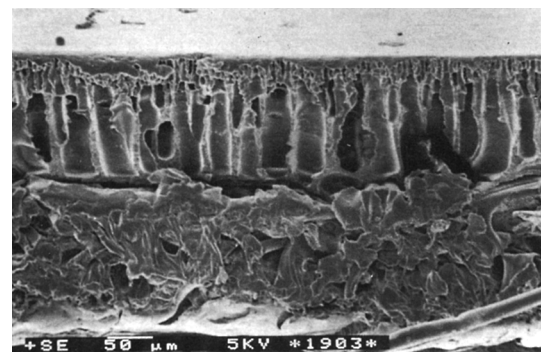
Figure 5 Effect of formamide concentration on porosity of membranes obtained from 16 mass % PAN solutions.



(a)



(b)



(c)

Figure 6 SEM of cuts of membranes obtained from 16 mass % PAN solution at different formamide concentrations: (a) 0%; (b) 2%; (c) 4 %.

Formamide, therefore, is a coagulant hindering the ability of DMF to dissolve PAN and so viscosity increases up to a certain limit. At a given concen-

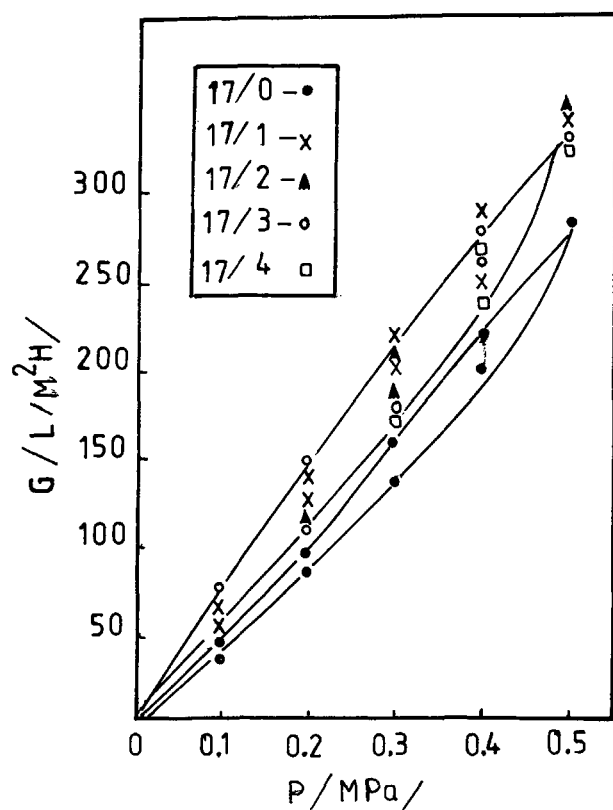


Figure 7 Effect of pressure and formamide concentration in the polymer solution on membrane efficiency.

tration of formamide, conditions occur for phase formation. Phase transition in this case is not abrupt. It takes place in a wide concentration interval, and gel and low molecular fractions are formed. A rotation viscometer was used to measure the decrease in dynamic viscosity. The curves in Figure 2 confirm this transition and show increasing viscosity rates at small angles of shear stress (τ/Pa). This indicates a structural arrangement of the polymer chains and the other components in the polymer solution. Due to the presence of nitrile groups, this polymer undergoes polymer-analogous reactions.^{8,9}

The enthalpies of the three polymer solutions pass through a maximum (Fig. 3) and show that up to this maximum the bond strength of the structures formed increases. After that, it decreases due to formation of microphases. It was calculated that entropy increases all the time, which indicates a decrease in the stability of the system. The enthalpies and entropies of the systems were calculated from the viscosity of the solutions at different temperatures.

Membranes were cast from all polymer solutions. The variation of the concentration of formamide re-

sulted in membrane structures which do not differ in pore-size distribution in the transport zone of the membranes (Fig. 4). The established dependence is characteristic for asymmetric structures. Three groups of pores with equivalent radii from 5000 to 500,000 E, 800 to 2000 E, and 250 to 500 E were formed. For the second group of pores, the ratio $\Delta V/\Delta \log R$ passes through a maximum when increasing the formamide concentration. This maximum corresponds to membranes obtained from solutions containing 1% formamide. The viscosity of these solutions has a maximum, too, which shows that there is a dependence between the polymer solution viscosity and the membrane structure. More pores with equal radii are formed from solution having greater viscosity. A decrease in viscosity results in a decrease in the number of these pores. The dependence of porosity (W) on pore radius ($\log R$) supports these results (Fig. 5). The S-shaped curves show that porosity changes abruptly when pore radius is from 900 to 1000 E. In the presence of formamide, the interval of abrupt changes in porosity increases. These results are proved also by the

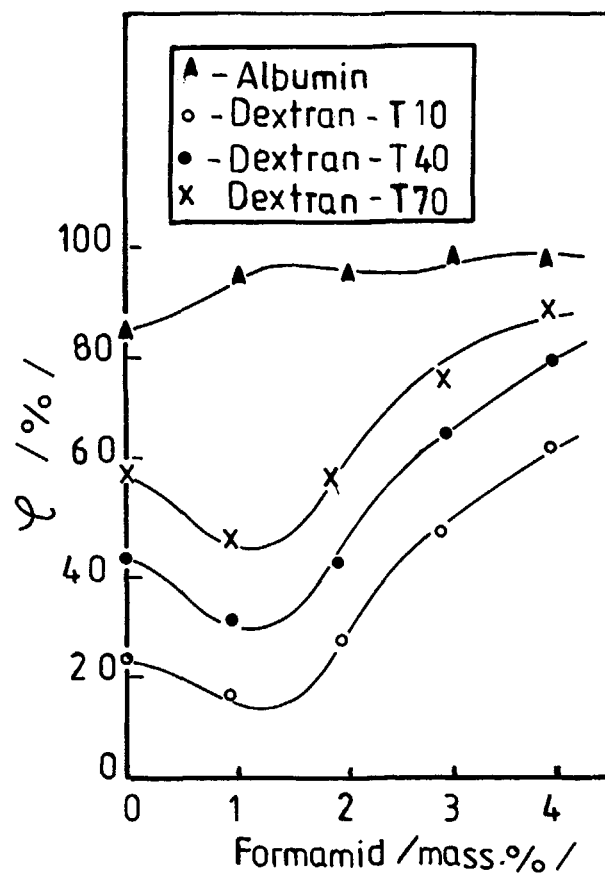


Figure 8 Effect of formamide concentration on membrane selectivity toward different calibration substances.

membrane structures shown in Figure 6. Increasing formamide concentration leads to changes in the microstructure of the membrane polymer film. The shorter fingerlike pores become longer and occupy the greater part of the layer. The result is a relative shift of the selective layer toward the surface of the membrane. These structural changes have a good effect on membrane efficiency and selectivity. The efficiency of membranes containing formamide is by 50–60 L/m² h higher than that of membranes without formamide, and this result is important for practical application (Fig. 7).

The optimum concentrations of formamide in the solutions can also be determined depending on membrane selectivity (Fig. 8). The selectivity was found to be the same for albumin and increased for dextran at formamide concentrations about 3 mass %. This concentration coincides with the maxima of the viscosity of polymer solutions. The differences observed in membrane selectivity toward dextran and albumin were attributed to the nature and configuration of their macromolecules.

Our former studies² show that similar selectivity can be achieved by using solutions containing more than 18 mass % polymer. The presence of formamide in the solutions provides a possibility to obtain membranes with the same good selectivity characteristics from solutions of lower polymer concentration. Lower polymer concentration leads to a better water transport through membranes.

The present research shows that membranes of optimum efficiency and selectivity can be formed on the basis of solutions of PAN in DMF in the presence of formamide. This result was obtained by utilizing the possibility to change the phase state of the polymer solution by using formamide.

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